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Herbicide transport to surface runoff from a claypan soil: Scaling from plots to fields

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Abstract: Streams and drinking water reservoirs throughout the claypan soil region of Missouri and Illinois are particularly vulnerable to herbicide contamination from surface runoff during spring. This study follows a plot-scale study conducted on claypan soils to quantify and compare edge-of-field herbicide losses from a corn–soybean rotation under mulch tillage and no-tillage systems. The objectives of the present study were to confirm at field scale (34.4 ha [85 ac] and 7.8 ha [19.3 ac]) the plot-scale findings (0.37 ha [0.92 ac]) on the effects of tillage and herbicide incorporation on herbicide transport and to evaluate the applicability of plot-scale exponential models in calculating atrazine and metolachlor concentrations as a function of application rate, runoff volume, and days after application at the field scale. Herbicide transport to surface runoff was studied (1997 to 2001) from two fields with cropping systems similar to those on the plots. Field 1 (F1) was a mulch tillage corn–soybean rotation system with surface-applied herbicides, which are then incorporated. Field 2 (F2) was a no-tillage corn–soybean rotation system with surface-applied herbicides that were not incorporated. During each event, runoff volumes were measured, and water samples were collected and analyzed for atrazine and metolachlor concentrations. The percentages of applied atrazine and metolachlor transported to surface runoff from no-tillage (F2) were 3.2 and 2.0 times those from mulch tillage (F1), respectively. Throughout the study period, 1.0% and 3.2% of total atrazine and 1.0% and 2.0% of total metolachlor applied to F1 and F2 were lost to surface runoff, respectively. Similar to the results from the plot study, the model performed well in calculating field atrazine concentrations from both mulch and no-tillage systems with coefficient of determination ≥ 0.70 and Nash and Sutcliffe efficiency ≥ 0.64. However, model performance in calculating metolachlor concentrations was poor for both tillage systems (Nash and Sutcliffe efficiency < 0.35). When the model was modified to include cumulative temperature instead of days after application, performance in calculating atrazine and metolachlor concentrations was improved, particularly metolachlor concentrations at the field scale. The coefficient of determination and Nash and Sutcliffe efficiency values for metolachlor relative to cumulative temperature and days after application were 0.62 and 0.61 versus 0.41 and –0.13 for F1, and 0.73 and 0.55 versus 0.53 and 0.34 for F2, respectively. Overall, the study confirmed plot-scale results that atrazine concentrations and losses were greater for a no-tillage system than for a mulch-tillage system, in which the herbicide was incorporated. The study also showed that the model developed using plot-scale data was applicable in calculating concentrations at the field scale, particularly for atrazine.

Key words: atrazine—metolachlor—mulch tillage—no-tillage—scaling

The Midwest Region of the United States produces 80% of the nation's corn (*Zea mays* L.) and soybean (*Glycine max* [L.] Merr.) and is a primary user of fertilizers and pesticides (Ward et al. 1994). For these grain crops, atrazine and metolachlor are two commonly used herbicides for weed control. In the Midwest, the off-site movement of herbicides into streams, rivers, and other surface water supplies is a serious nonpoint source pollution problem. Soils, such as the claypan soils (Vertic Epiaqualfs and Vertic Albaqualfs), which have a significant runoff potential because of low permeability, are especially susceptible to soil and herbicide losses with runoff. Early knowledge of this problem sparked the research community to study the factors that influence herbicide movement and transport in surface runoff (Blanchard and Lerch 2000; Lerch and Blanchard 2003). Plot and field-scale studies were conducted to evaluate factors that influence herbicide transport to surface runoff, including tillage type (Triplett et al. 1978; Baker and Johnson 1979; Sauer and Daniel 1987; Gaynor et al. 1995), incorporation (Baker and Laflen 1979; Hall et al. 1983; Mickelson et al. 1997), residue management (Kenimer et al. 1987), and timing of the runoff event related to herbicide application (Fawcett et al.1994; Shipitalo et al. 1997; Hansen et al. 2001). Studies were also conducted at the watershed scale to identify the magnitude of herbicide concentrations and loads from agricultural practices (Wauchope and Leonard 1980; Wu et al. 1983; Ng and Clegg 1997; Blanchard and Lerch 2000; Capel et al. 2001; Lerch and Blanchard 2003).

Several studies have shown that tillage systems that leave residues on the soil surface in order to control soil erosion also reduce surface runoff (Laflen et al. 1978; Larson et al. 1978; Johnson and Moldenhauer 1979; Langdale et al. 1979; McGregor and Greer 1982) and herbicide loss to surface runoff (Triplett et al. 1978; Baker and Johnson 1979; Kenimer et al. 1987). Others have indicated that a no-tillage system, which leaves all residues on the ground, does not always reduce runoff (Siemens and Oschwald 1976; Lindstrom et al. 1981; Ghidey and Alberts 1998) and may even result in increased herbicide loss. In addition, lower runoff did not always imply lower herbicide losses. In some cases, the reduction in runoff was offset by an increase in herbicide concentration (Sauer and Daniel 1987) and resulted in no significant effect of tillage on herbicide losses. Herbicide concentrations were also found to increase with increasing amounts of residue on the ground surface for any tillage system (Kenimer et al. 1987).

Incorporation of herbicide was consistently associated with significant reductions of herbicide losses and concentrations compared to broadcast applications (Baker and

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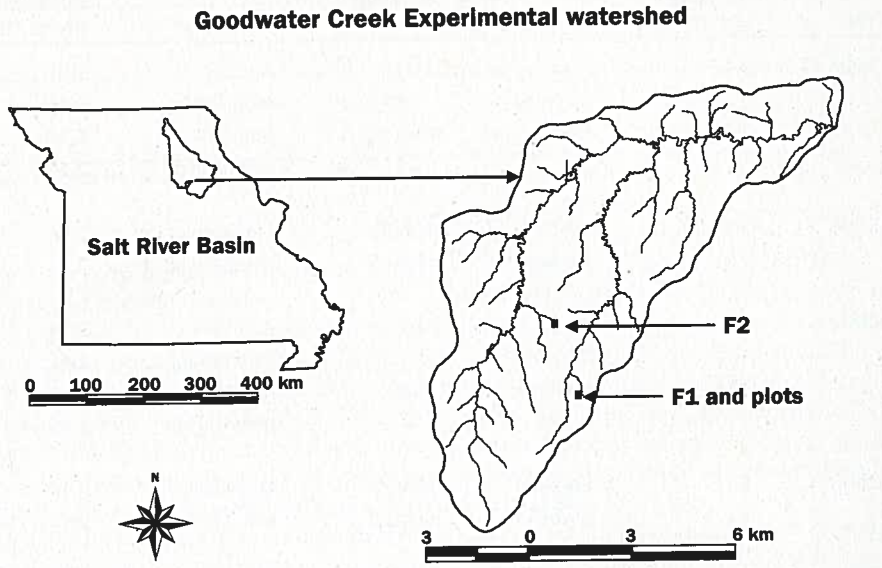
Laflen 1979; Hall et al. 1983; Capel et al. 2001). Capel et al. (2001) suggested that incorporation of herbicides is the simplest and most effective means of reducing herbicide transport in surface runoff.

All the plot and field scale studies, except those that used rainfall simulators (Baker and Laflen, 1979; Kenimer et al., 1987; Sauer and Daniel, 1987), indicated that timing of runoff event relative to herbicide application date was a critical factor that controlled the loss of herbicide. Ghidey et al. (2005) reported that herbicide concentrations in surface runoff were very high when a runoff occurred shortly after application and that most of the annual herbicide loss occurred during the first two events following herbicide application.

Long-term effects of various cropping and management systems on surface runoff and soil loss have been studied using natural rainfall erosion plots on Mexico silt loam, a common claypan soil series in northeastern Missouri (Alberts et al. 1985; Ghidey and Alberts 1998). The long-term (12 year) study on the effects of cropping and management indicated that no-tillage increased mean annual runoff by 11% and 25%, compared to moldboard plow and chisel plow, respectively, during the crop growing season (Ghidey and Alberts 1998). However, cropping and management effects on surface water quality in the Midwest claypan soil region have not been thoroughly assessed. This study was part of a broad research effort conducted to develop environmentally sound, economically profitable, and socially acceptable cropping systems and technologies for claypan and claypan-like soils. The study was conducted at Goodwater Creek watershed (figure 1) located in the southern portion of the Central Claypan Region (Major Land Resource Area 113), an area of about 3 million ha (8 million ac) in Missouri and Illinois (USDA NRCS 2006). Soil and water quality concerns in this area include the high to very high runoff potential of claypan soils, which are characterized by a clay layer that restricts infiltration 15 to 45 cm (6 to 18 in) below the surface (Lerch et al. 2008). Measured infiltration rates on the claypan range from a few micrometers per hour to less than a millimeter per day (Blanco-Canqui et al. 2002). Thus, herbicide leaching risks are minimal, but transport by runoff is significant. Research has been conducted on watershed, field, and plot scales to evaluate the effects of various farming systems on surface water quality at Goodwater Creek watershed. The effect of cropping systems on herbicide loss in surface runoff from the plot scale has been previously reported by Ghidey et al. (2005). They found that atrazine and metolachlor losses from plots under no-tillage cropping systems, where herbicide was surface applied and not incorporated, were 2.2 and 1.6 times those from plots under mulch tillage, where herbicide was surface applied and incorporated. A generalized model that predicts herbicide concentrations in surface runoff as a function of application rate, runoff volume, and days after application was developed and tested using the data from the plot-scale study.

To complete the assessment of cropping and management effects on water quality, the plot-scale results needed to be extended to larger scales using available field-scale data. In this paper, runoff and herbicide data measured from two field-case studies are reported. The specific objectives of this study were (1) to confirm at field scale the results found from the plot-scale study on the effects of tillage on herbicide transport in surface runoff, (2) to evaluate the applicability of the plot-scale exponential model for the calculation of atrazine and metolachlor concentrations at the field scale, and (3) to modify the exponential model by inserting a temperature variable and testing its applicability at both plot and field scales.

Figure 1
Location of the research fields and plots. F1 is Field 1 and F2 is Field 2.



Materials and Methods

The study was located in the Goodwater Creek watershed, a 7,299.0 ha (18,036.2 ac) agricultural area in the claypan soil region of north-central Missouri (figure 1). Field-scale case studies were conducted on two fields (Field 1 [F1] and Field 2 [F2]) located within 5 km (3.1 mi) of each other with similar characteristics in soils and landscape relief. The drainage areas of F1 and F2 were 34.4 and 7.8 ha (85.0 and 19.3 ac), respectively. Predominant soils are Vertic Epiaqualfs, Vertic Albaqualfs, and Vertic Epiaqualfs of the Mexico, Adco, and Leonard series, respectively, (USDA NRCS 2010) three soil series that are extensive within the Central Claypan Area. The mapping units of these soils belong to the soil order of alfisols and are considered poorly drained because of the presence of the claypan layer. The clay content of the claypan layer is generally about 50% or greater, and the clays are primarily smectites. Field slopes ranged from 0% to 3%.

Crop rotation and herbicide management of F1 and F2 from 1997 to 2001 are listed in table 1. Field 1 was under a mulch tillage corn–soybean rotation where herbicides were surface applied and incorporated. Mulch tillage consisted of spring disc plowing or field cultivation before planting and field cultivation for herbicide incorporation. Field 2 was in a no-tillage corn–soybean rotation where herbicides were surface applied but were not incorporated. Corn was planted during the

Table 1
Tillage and herbicide management information for Field 1 (F1) and Field 2 (F2).

Year	Farming system	Crop	Planting date	Herbicide*	Application rate (kg ha^{-1})	Date of application	Tillage
1997	F1	Corn	May 6	Atrazine	2.46	May 6	Mulch tillage
				Metolachlor	2.15	May 6	
	F2	Corn	May 10	Atrazine	2.46	May 10	No-tillage
				Metolachlor	2.15	May 10	
1998	F1	Soybean	May 25	Metolachlor	2.14	May 23	Mulch tillage
	F2	Soybean	May 29	Metolachlor	2.14	May 27	No-tillage
1999	F1	Corn	May 24	Atrazine	2.24	May 23	Mulch tillage
				Metolachlor	1.42	May 23	
	F2	Corn	May 25	Atrazine	2.24	May 23	No-tillage
				Metolachlor	1.42	June 3	
2000	F1	Soybean	May 21	Metolachlor	2.14	May 16	Mulch tillage
	F2	Soybean	May 23	Metolachlor	2.14	May 17	No-tillage
2001	F1	Corn	April 28	Atrazine	2.24	April 27	Mulch tillage
				Metolachlor	2.20	April 27	
	F2	Corn	April 27	Atrazine	2.07	April 25	No-tillage
				Metolachlor	1.61	April 25	

* Other herbicides (preplant, at planting, or post plant) may have also been used to control weeds but are not reported here because they were not part of the water quality monitoring.

odd years, and both atrazine and metolachlor were applied. Only metolachlor was applied when soybean was planted.

The outlets of F1 and F2 were instrumented with concrete v-notch weirs, water stage recorders, and refrigerated automated samplers (ISCO 3230, Teledyne Isco, Inc., Lincoln, Nebraska) to measure runoff and collect runoff samples for chemical analysis. Electronic head measurements were recorded at 5-minute intervals, and all flow data were aggregated to average daily or event runoff. The flow-paced sampling technique was used to collect runoff samples. A maximum of 24 bottles were collected per runoff event. In each bottle, up to three 100 mL (3.4 oz) sips were collected at a flow depth interval of 0.82 mm (0.032 in) for F1 and 1.8 mm (0.071 in) for F2. If events were large enough to fill all bottles, samples were collected, and bottles were replaced. When runoff events were not large enough to trigger automatic sampling, either grab samples were collected or concentrations for the unsampled events were estimated using linear interpolation. Samples were transferred to the laboratory on ice within 48 hours of collection and were stored in a cold room at 2°C to 4°C (36°F to 39°F).

Precipitation was measured using rain gauges (Universal Recording Rain Gage Model 5-780, Belfort Instrument) installed at F1 and F2. The gauges were modified with a load cell and data logger to automate the measurement. Rainfall was directed through a 20 cm (7.9 in) diameter collecting ring and funnel to a bucket resting on the surface of the load cell that was connected to the data logger for recording rainfall volumes every two minutes.

Air and soil temperatures were measured from a weather station located at F1. Air and soil temperature were collected on Campbell Scientific 21X data logger. Air temperature data was measured using a Campbell Scientific model HMP35C installed 2 m (6.6 ft) above ground level. Soil temperature was measured using a Campbell model 107b soil probe installed at a depth of 10 cm (4 in) under sod. All sensors were sampled every 60 seconds, and averages were stored in memory every hour.

The results of this study (both hydrology and herbicide data) were analyzed by dividing each year into two periods: the Crop Growing Season (CGS) period, which included runoff events that occurred from the spring tillage operation prior to planting until harvest (April to September) and the Fallow period, which included events prior to the tillage operation before planting (January to March) and after harvest (October to December).

Herbicide Analysis and Load Computation. Samples were refrigerated until processing. All samples were filtered through 0.45 µm (17.72 µin) nylon filters and were analyzed for atrazine and metolachlor using enzyme-linked immuno sorbent assays (ELISA) (Strategic Diagnostics Inc., Warminster, Pennsylvania). Limits of detection were 0.05 µg L^{-1} for both herbicides. Runoff samples from the first two events were diluted as needed to ensure that concentrations fell within the linear range (0.05 to 5 µg L^{-1}) of the ELISA kits.

For each event, individual sample concentrations (µg L^{-1}) were multiplied by corresponding runoff volumes (L) to calculate herbicide load. Herbicide losses (g ha^{-1}) were calculated by dividing the computed load by the area of the field. Seasonal flow-weighted concentrations were based on the seasonal herbicide load and the seasonal runoff volume.

Description of Plot Study. Runoff and herbicide concentrations in runoff were mea-

Table 2
Coefficients (α and *k* values) of the exponential model (equation 1) obtained during the plot study (Ghidey et al. 2005). The r^2 and E_{NS} are the coefficient of determination and Nash and Sutcliffe efficiency values between measured and calculated concentrations.

	Atrazine				Metolachlor			
	α	κ	r^2	E_{NS}	α	κ	r^2	E_{NS}
CS1	0.0232	0.1087	0.68	0.67	0.0203	0.0862	0.71	0.70
CS2	0.0959	0.1412	0.80	0.79	0.0110	0.0678	0.23	0.16

Note: CS1 = plot study with mulch tillage. CS2 = plot study with no-tillage.

sured from plots located next to F1 (figure 1) and were reported by Ghidey et al. (2005). In 1991, six cropping systems were established on thirty 0.37 ha (0.92 ac) plots (20 m [65 ft] wide by 189 m [620 ft] long), in a randomized complete block design with three replications. Two of the cropping systems studied at the plot scale were mulch tillage (CS1), similar to F1, and no-tillage (CS2), similar to F2. From 1997 until 2001, the outlets of the plots under CS1 and CS2 planted to corn were instrumented with Parshall flumes and automatic samplers to measure runoff volume and collect runoff samples for chemical analysis. The flumes were ASTM-standard Parshall flumes (Culverts & Industrial Supply Co., Mills, Wyoming), with nominal 0.1524 m (6 in) throats and were installed according to manufacturer's specifications. Automated samplers (Sigma 900MAX, America Sigma, Inc., New York) were installed annually right after planting. The study was designed to be able to sample up to a 5.08 cm (2 in) runoff event. Each sampler had eight bottles, and each bottle collected up to 6.35 mm (0.25 in) of runoff. To capture small events, up to nine subsamples were collected into each bottle, each representing 0.706 mm (0.0278 in) of runoff. The samples were transported on ice back to the laboratory.

Modeling Herbicide Concentration. The model that was tested using atrazine and metolachlor concentration data from plots (Ghidey et al. 2005) is an exponential equation (equation 1) that accounts for the effects of time after application, runoff volume, and application rate on herbicide concentration in surface runoff. In this study, the applicability of the model to field-scale data was evaluated:

$$[C] = \alpha \times \left(\frac{R}{Q}\right) \times e^{-(\kappa \times t)} , \quad (1)$$

where $[C]$ is computed atrazine or metolachlor concentration (μg L^{-1}), R is the herbicide application rates (μg ha^{-1}), Q is the runoff measured for the events (L ha^{-1}), t is the time after herbicide application (days), and α and κ are coefficients.

Ghidey et al. (2005) indicated that the model was not able to correctly calculate herbicide concentrations when there were multiple events in a day, especially when the runoff from the second event was much lower than the first event. To avoid this problem, only runoff events greater than 2 mm (0.08 in) were considered. The same approach was also taken for the validation of plot-scale model to field data.

Previous studies indicated that biological processes that control herbicide degradation are strongly influenced by temperature (Dinelli et al. 2000; Jackson 2003). Their studies indicated that lower temperature significantly decreased degradation rate. To evaluate the effect of temperature, equation 1 was modified to include a cumulative temperature parameter instead of time after herbicide application:

$$[C] = \alpha \times \left(\frac{R}{Q}\right) \times e^{-(\kappa \times T_{cum})} , \quad (2)$$

Where T_{cum} is the cumulative value of the average of the minimum and maximum daily air and soil temperatures starting at the date of herbicide application until the day the event occurred. T_{cum} is computed as

$$T_{cum} = \sum_{i = t_{appl}}^{i = t_{event}} \frac{T_i^{Amax} + T_i^{Amin} + T_i^{Smax} + T_i^{Smin}}{4} , \quad (3)$$

where Ti^{Amax} is the maximum daily air temperature (°C), Ti^{Amin} is the minimum daily air temperature (°C), Ti^{Smax} is the maximum daily soil temperature (°C), Ti^{Smin} is the minimum daily soil temperature (°C), t_{appl} is the herbicide application date, and t_{event} is the runoff event date.

These temperatures were available in our data set and were used as a surrogate for the mean daily temperature of the surface soil layer where atrazine was applied. The number of days between application and the runoff event is implicitly included in this equation.

Validation of the Plot-Scale Model at the Field Scale. In the plot-scale study, the parameters α and κ for equation 1 had been determined for atrazine and metolachlor on CS1 and CS2 (table 2). The model coefficients were used to calculate atrazine and metolachlor concentrations from F1 and F2 to evaluate the applicability of the model at a field scale.

The nonlinear procedure of Statistical Analysis Systems (Proc NLIN) was run to compute the coefficients α and κ of equation 2 for both atrazine and metolachlor using the plot-scale data (SAS 2002-2003). Then the application of these coefficient values to the larger scale was tested.

The performance of the models (equations 1 and 2) was evaluated by comparing measured and simulated loads and concentrations using two methods: (1) the coefficient of determination (r^2) and (2) the model efficiency using the Nash and Sutcliffe efficiency (E_{NS}) (1970) calculated with the following equation:

$$E_{NS} = 1 - \frac{\sum_{t=1}^{n}(Q_m^t - Q_c^t)^2}{\sum_{t=1}^{n}(Q_m^t - Q_{av})^2} , \quad (4)$$

where E_{NS} is the efficiency of the model, Q^t_m is the measured value at time t, Q^t_c is the calculated value at time t, Q_{av} is the average of the measured values, and n is the number of observations.

The E_{NS} value indicates how well the plot of observed versus calculated values fits the 1:1 line. An E_{NS} value of 1 indicates a perfect 1:1 relationship between measured and simulated values. A value less than zero indicates that the average value of the observed time series would have been a better predictor than the model.

Results and Discussion

Precipitation and Surface Runoff. Annual and seasonal precipitation and surface runoff are shown in figure 2. The five-year (1997 to 2001) mean annual precipitation at F1

Figure 2

Annual and seasonal precipitation and runoff measured from Field 1 (F1) and Field 2 (F2). The dashed line represents 37-year mean annual precipitation for Goodwater Creek watershed. The graphs show (a) annual precipitation, (b) annual runoff, (c) Crop Growing Season Period precipitation, (d) Crop Growing Season Period runoff, (e) Fallow Period precipitation, and (f) Fallow Period runoff.

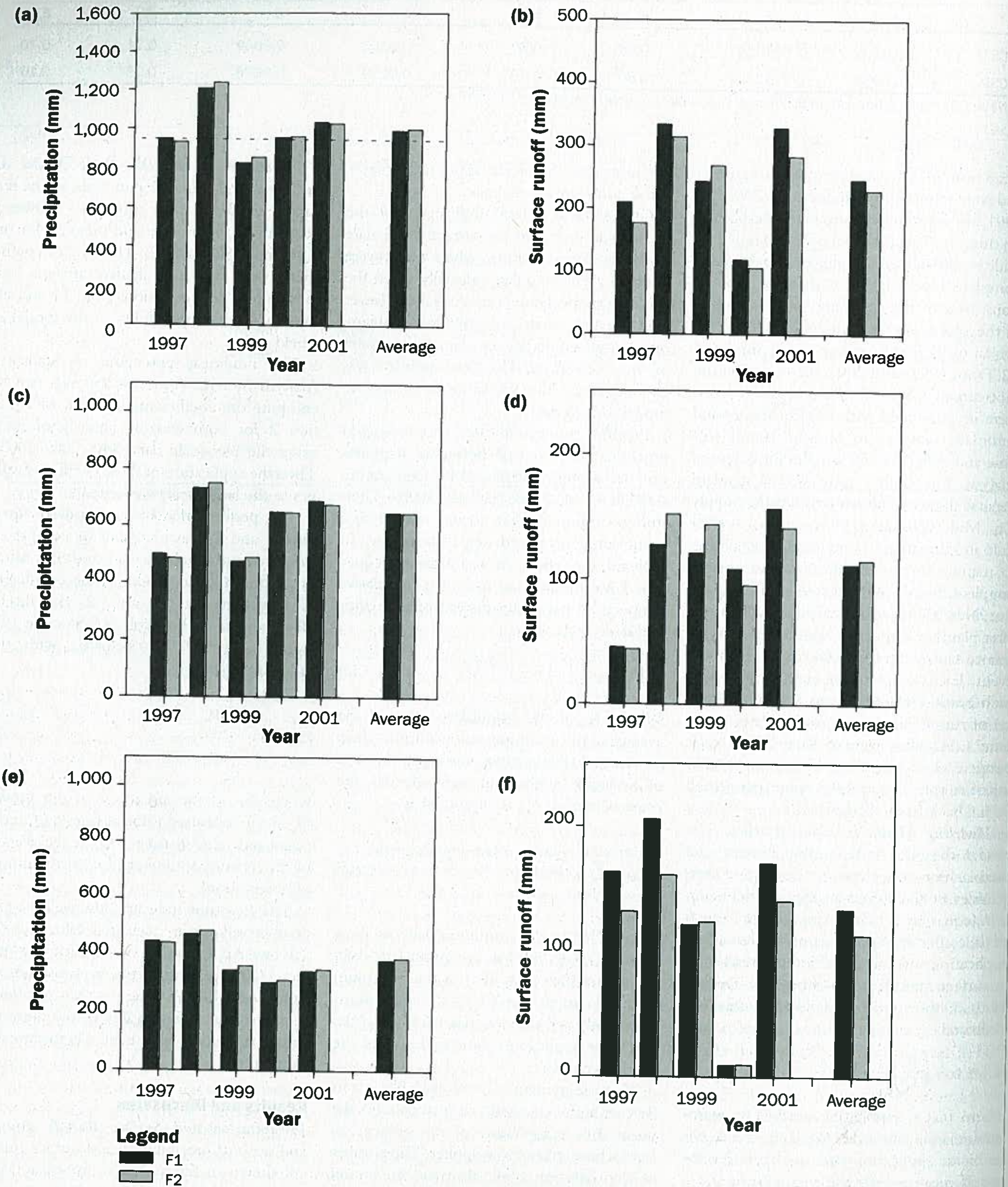


Table 3
Annual atrazine and metolachlor losses from Field 1 (F1) and Field 2 (F2).

	Atrazine				Metolachlor			
	F1		F2		F1		F2	
Year	Losses (g ha^{-1})	Percent of applied	Losses (g ha^{-1})	Percent of applied	Losses (g ha^{-1})	Percent of applied	Losses (g ha^{-1})	Percent of applied
1997	32.6	1.3	107.8	4.4	34.0	1.6	65.0	3.0
1998	na	na	na	na	24.4	1.1	71.8	3.4
1999	11.2	0.5	31.6	1.4	10.6	0.7	10.6	0.7
2000	na	na	na	na	4.7	0.2	2.9	0.1
2001	27.5	1.3	75.6	3.7	21.9	1.0	33.6	2.1
Total	71.3	1.0*	215.4	3.2*	95.6	1.0*	183.9	2.0*

Note: na = indicates that herbicide was not applied that year.
* These are the percent of the total herbicides applied from 1997 to 2001.

and F2 was 1,009 and 1,001 mm (39.7 and 39.4 in), respectively, slightly more than the long term (37 year) mean annual precipitation of 949 mm (37.4 in) for Goodwater Creek watershed. At both study areas, approximately 65% of the mean annual precipitation occurred during the CGS. Rainfall events that occurred during the CGS period resulted in only two runoff events in 1999. Rainfall events in 2000 resulted in little or no runoff during the CGS period, except one event that occurred on August 23, 2000, that produced 73 and 67 mm (2.9 and 2.6 in) of runoff from F1 and F2, respectively.

The 1997 to 2002 mean annual runoff from mulch tillage (F1) and no-tillage (F2) were 249 and 238 mm (8.5 and 8.4 in), representing 25% and 22% of the total rainfall, respectively. The mean surface runoff values for the CGS period measured at F1 and F2 were similar (114 mm [4.5 in] at F1 and 118 mm [4.7 in] at F2). The difference in surface runoff between F1 and F2 during the critical period for herbicide loss (April to June) was small (<1%).

In this study, no-tillage (F2), despite leaving all residues on the surface, was not shown to reduce runoff, particularly during the CGS period, as indicated in some studies (Laflen et al. 1978; Larson et al. 1978; Johnson and Moldenhauer 1979; Langdale et al. 1979; McGregor and Greer 1982). During the CGS period, F1 had tillage operations, including spring disc plowing or field cultivation before planting and field cultivation for herbicide incorporation. Both tillage and residue are expected to reduce surface runoff. Tillage breaks the surface soil seal, increases microrelief and soil drying, and as a result, increases infiltration and reduces surface runoff. Residue is also expected to increase infiltration and reduce surface runoff by preventing the development of surface crusting and slowing down runoff due to residue on the ground, thus giving it more time to infiltrate. In this study, surface runoff measured from F1 and F2 was similar, possibly because the effect of tillage associated with the mulch tillage system (F1) was countering the effect of residue associated with no-tillage (F2) in reducing surface runoff. Ghidey et al. (2005) reported similar results from the plot-scale study where the difference in mean seasonal runoff (1997 to 2002) from no-tillage plots and mulch-tillage plots was not significantly different.

Herbicide Losses from the Fields. Annual atrazine and metolachlor losses are given in table 3. For the years that atrazine was applied (1997, 1999, and 2001), losses in surface runoff were 1% of applied for F1 and 3.2% of applied for F2. Total metolachlor loss was 1% from F1 and 2% from F2. Overall, during the study period, the percentages of applied atrazine and metolachlor lost to surface runoff from F2 were 3.2 and 2 times those from F1, respectively. Ghidey et al. (2005) found similar results on the plot scale study, where percent of applied atrazine and metolachlor losses from no-tillage were 2.2 and 1.6 times those from mulch tillage.

For individual years, the percent of applied atrazine lost to surface runoff from F2 was 3.4, 2.8, and 2.9 times that from F1 in 1997, 1999, and 2001, respectively. The percent of applied metolachlor lost to runoff from F2 was 1.9, 3.1, and 2.1 times that from F1 in 1997, 1998, and 2001, respectively. In 2000, only a few small runoff events were measured from either field during the first few weeks following metolachlor application, and as a result, metolachlor losses from both were small. In 1999, only two events occurred during the CGS period, and metolachlor losses from both fields were small and similar.

Most of the herbicide losses occurred during the first two events following herbicide application. For instance, in 1997, the first two events, which occurred within three weeks after application, accounted for more than 93% of the annual atrazine and metolachlor losses from both F1 and F2. In 2001, the first event that occurred within a week of herbicide application accounted for 82% and 86% of the annual atrazine losses from F1 and F2, respectively. These findings were consistent with previous studies that reported that most herbicide losses in surface runoff occurred within a few weeks after application (Fawcett et al. 1994; Shipitalo et al. 1997; Hansen at al. 2001).

Herbicide loss can be affected by the volume of runoff and incorporation. In this study, the difference in the volume of runoff measured during the critical herbicide loss period (April to June) between F1 and F2 was less than 1%, indicating that volume of runoff did not play an important role in herbicide loss to runoff. Thus, the difference in herbicide loss between the mulch tillage and no-tillage was mainly due to incorporation. Incorporation of herbicide below the layer of a mixing zone (0 to 2 cm [0 to 0.8 in] of the soil profile) (Ahuja and Lehman 1983) can significantly reduce herbicide concentration and losses in surface runoff. Hall et al. (1983) reported that incorporation reduced atrazine runoff losses during the growing season by 74%. In this study, atrazine and metolachlor losses from mulch tillage were 64% and 48% less than those from no-tillage. Thus, for claypan soils, the lack of herbicide incorporation associated with no-tillage increased herbicide loss to surface runoff, compared to farming systems that incorporate soil-

Table 4
Event runoff and concentrations of atrazine and metolachlor measured from Field 1 (F1) and Field 2 (F2).

	Runoff (mm)		Atrazine (μg L^{-1})		Metolachlor (μg L^{-1})	
Date	F1	F2	F1†	F2†	F1†	F2†
05/19/97	0.0	0.6*	nr	1,712.0 (9)	nr	808.7 (9)
05/26/97	10.9	17.6	224.0 (20)	512.1 (16)	200.2 (20)	320.1 (16)
05/29/97	4.5	0.0	142.3 (23)	nr	220.2 (23)	nr
06/15/97	0.3‡	0.3‡	59.5 (40)	74.1 (36)	86.2 (40)	69.1 (36)
06/22/97	12.3	11.6	13.3 (47)	60.0 (43)	14.8 (47)	30.0 (43)
06/08/98	5.7	8.0	na	na	166.8 (16)	360.2 (12)
06/14/98	13.2	19.0	na	na	65.6 (22)	127.3 (18)
06/21/98	10.0	15.4	na	na	18.9 (29)	38.4 (25)
06/29/98	38.5	34.4	na	na	5.1 (37)	16.7 (33)
07/04/98	23.1	43.4	na	na	4.0 (42)	11.7 (38)
07/07/98	0.4‡	1.9	na	na	6.4 (45)	14.8 (41)
07/10/98	0.1‡	1.1	na	na	7.6 (48)	6.8 (44)
07/30/98	5.2	4.2	na	na	3.1 (68)	5.9 (64)
06/23/99	4.0	6.9	95.5 (31)	87.6 (31)	43.7 (31)	28.4 (20)
06/30/99	24.0	44.6	28.4 (38)	57.2 (38)	35.1 (38)	17.8 (27)
05/26/00	0.8	0.1‡	na	na	24.3 (10)	9.6 (9)
06/11/00	1.9	0.1‡	na	na	5.0 (26)	11.6 (25)
06/14/00	4.7	0.9‡	na	na	18.4 (29)	11.5 (28)
06/20/00	14.2	8.0	na	na	16.9 (35)	13.1 (34)
06/24/00	0.2‡	1.4	na	na	13.9 (39)	9.4 (38)
06/25/00	8.2	8.6	na	na	5.6 (40)	7.3 (39)
05/03/01	6.6	8.5	338.8 (6)	759.3 (8)	125.3 (6)	274.6 (8)
05/19/01	7.3	10.9	29.2 (22)	56.6 (24)	58.4 (22)	49.6 (24)
05/21/01	5.3	0.2‡	1.3 (24)	71.0 (26)	22.9 (24)	44.5 (26)
06/01/01	20.3	16.8	2.9 (35)	8.7 (37)	4.3 (35)	6.4 (37)
06/06/01	66.6	60.4	3.1 (40)	4.9 (42)	10.5 (40)	5.4 (42)

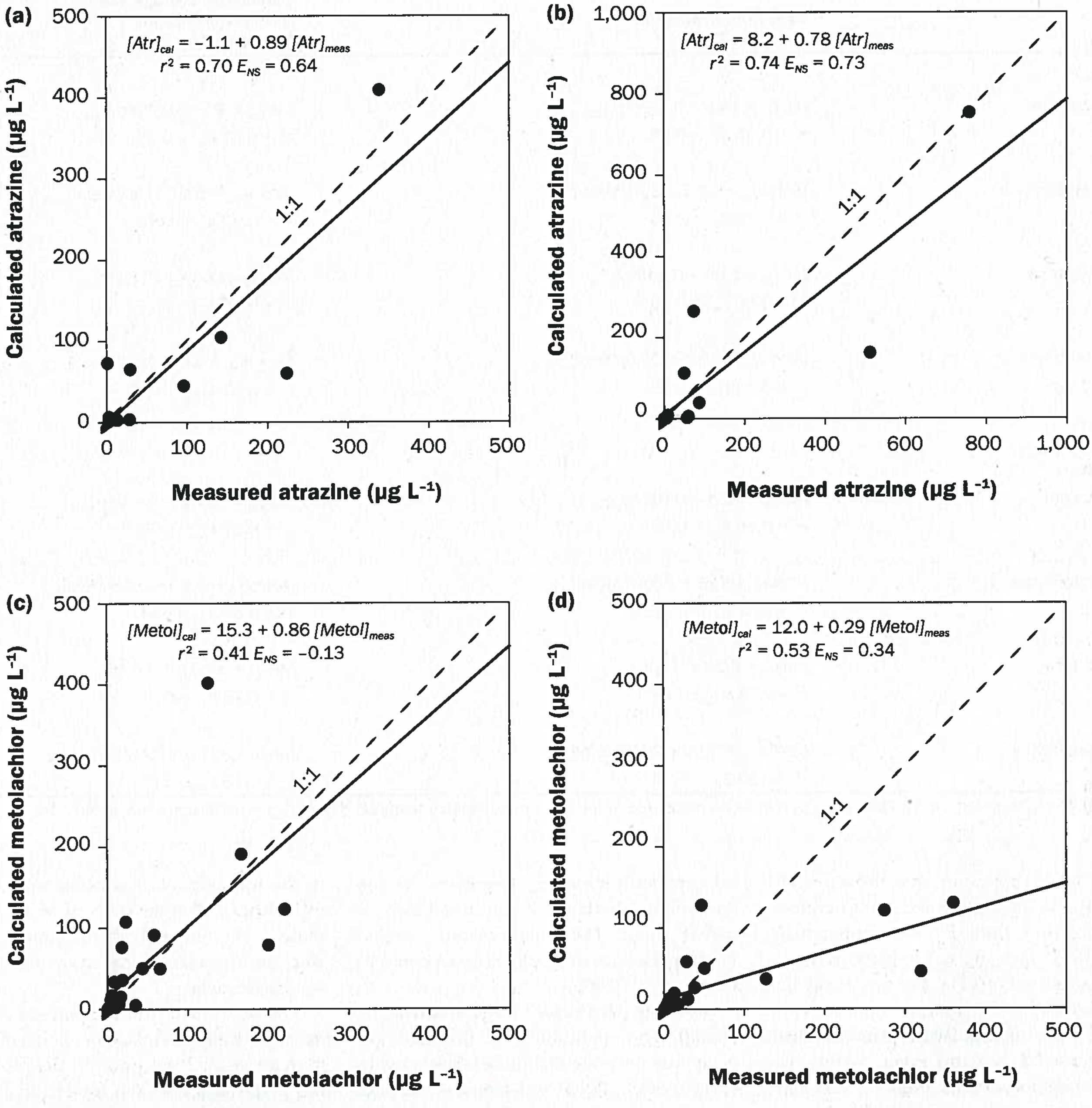
Notes: nr = herbicides were not measured for the event because there was no runoff. na = samples were not analyzed for atrazine concentration because atrazine was not applied.
* Indicates grab sample was collected because the event was not large enough to trigger automatic sampling.
† Numbers in parentheses in this column are days after herbicide application.
‡ Indicates concentrations were estimated for the event using linear interpolation.

applied herbicides. Additional research is needed to determine if these results can be generalized to other soils, with restrictive subsurface layers within ~50 cm (~20 in) of the surface (e.g., fragipans, high clay content argillic horizons).

Herbicide Concentrations in Surface Runoff. Flow-weighted herbicide concentrations for the events that occurred during the CGS and after herbicide application are shown in table 4. Samples were also collected for the events that occurred before herbicide application to check if any residues remained from previous years. Metolachlor was applied to both F1 and F2 each year during the study period, and concentrations for the events that occurred before application were small (ranged from 0.2 to 0.7 μg L^{-1}). Atrazine concentrations for the events that occurred prior to application in 1997, 1999, and 2001, or prior to planting in 1998 and 2000 were <1.0 μg L^{-1}, except for one event (April 14, 1999) where atrazine concentration in runoff was 2.2 μg L^{-1}. This could be due to high atrazine concentration in precipitation. Rainfall samples were collected from the station located at F1 from 1997 to 2002 to measure herbicide concentrations in precipitation (Ghidey et al. 2005). Atrazine and metolachlor concentrations were, in general, very low (<0.1 μg L^{-1}), particularly during the CGS period, and their contribution to surface runoff was considered negligible. However, for this event, atrazine concentration in precipitation was 1.1 μg L^{-1}.

During the CGS period, average flow-weighted atrazine and metolachlor concentrations measured from F2 were larger than those measured from F1. Average flow-weighted atrazine concentrations from F1 and F2 were 24.8 and 66.4 μg L^{-1}, and average flow-weighted metolachlor concentrations were 33.2 and 56.7 μg L^{-1}, respectively. Ghidey et al. (2005) found similar results in the plot-scale study, where

Figure 3
Comparison of atrazine and metolachlor concentrations measured at Field 1 (F1) and Field 2 (F2) to those calculated using the coefficients of the model (equation 1) generated using the plot-scale data: (a) atrazine in F1, (b) atrazine in F2, (c) metolachlor in F1, and (d) metolachlor in F2.



Notes: $[Atr]_{cal}$ = atrazine calculated. $[Atr]_{meas}$ = atrazine measured. $[Metol]_{cal}$ = metolachlor calculated. $[Metol]_{meas}$ = metolachor measured.

average flow-weighted atrazine and metolachlor concentrations measured from CS2 (no-tillage) were 100% and 50% larger than those measured from CS1 (mulch tillage).

As shown with plot data (Ghidey et al. 2005), time after herbicide application was an important factor affecting herbicide concentrations in runoff. Herbicide concentrations were very high for the first runoff event in 1997, 1998, and 2001 (table 4). In comparison, measured concentrations in 1999 and 2000 were relatively small. In 1999, the first event occurred three to four weeks after atrazine and metolachlor were applied to F1 and F2. In 2000, there was a relatively dry period from the end of April to mid-June; only a few rainfall events occurred within four weeks of herbicide application, and they produced little or no surface runoff. Throughout the study period, the highest concentration was observed in 1997 at F2 for a small runoff event (0.6 mm [0.024 in]) that occurred nine days after application. It did not produce any runoff on F1. For this event, atrazine and metolachlor concentrations from F2 were 1,712 and 809 μg L^{-1}, respectively.

Lack of herbicide incorporation at F2 resulted in greater atrazine and metolachlor concentrations for the first few events follow-

Table 5
Comparison of the coefficient of determination (r^2) and Nash and Sutcliffe efficiency (E_{NS}) values generated in calculating atrazine and metolachlor concentrations from the plots and fields using equations 1 and 2.

	Days after application (equation 1)	Cumulative average soil and air temperature (equation 2)
Plots		
CS1 Atrazine	$[Atr]_{est} = 11.5 + 0.69[Atr]_{meas}$ $r^2 = 0.68$ $E_{NS} = 0.67$	$[Atr]_{est} = 6.7 + 0.68[Atr]_{meas}$ $r^2 = 0.67$ $E_{NS} = 0.65$
CS1 Metolachlor	$[Metol]_{est} = 11.4 + 0.71[Metol]_{meas}$ $r^2 = 0.71$ $E_{NS} = 0.70$	$[Metol]_{est} = 6.0 + 0.82[Metol]_{meas}$ $r^2 = 0.72$ $E_{NS} = 0.72$
CS2 Atrazine	$[Atr]_{est} = 1.65 + 0.84[Atr]_{meas}$ $r^2 = 0.80$ $E_{NS} = 0.79$	$[Atr]_{est} = 17.4 + 0.75[Atr]_{meas}$ $r^2 = 0.72$ $E_{NS} = 0.72$
CS2 Metolachlor	$[Metol]_{est} = 19.4 + 0.30[Metol]_{meas}$ $r^2 = 0.23$ $E_{NS} = 0.16$	$[Metol]_{est} = 8.6 + 0.50[Metol]_{meas}$ $r^2 = 0.42$ $E_{NS} = 0.35$
Fields		
F1 Atrazine	$[Atr]_{est} = -1.1 + 0.89[Atr]_{meas}$ $r^2 = 0.70$ $E_{NS} = 0.64$	$[Atr]_{est} = -11.4 + 0.93[Atr]_{meas}$ $r^2 = 0.82$ $E_{NS} = 0.78$
F1 Metolachlor	$[Metol]_{est} = 15.3 + 0.86[Metol]_{meas}$ $r^2 = 0.41$ $E_{NS} = -0.13$	$[Metol]_{est} = 13.0 + 0.63[Metol]_{meas}$ $r^2 = 0.62$ $E_{NS} = 0.61$
F2 Atrazine	$[Atr]_{est} = 8.2 + 0.78[Atr]_{meas}$ $r^2 = 0.74$ $E_{NS} = 0.73$	$[Atr]_{est} = 32.0 + 0.77[Atr]_{meas}$ $r^2 = 0.78$ $E_{NS} = 0.78$
F2 Metolachlor	$[Metol]_{est} = 12.0 + 0.29[Metol]_{meas}$ $r^2 = 0.53$ $E_{NS} = 0.34$	$[Metol]_{est} = 4.4 + 0.45[Metol]_{meas}$ $r^2 = 0.73$ $E_{NS} = 0.55$

Notes: $[Atr]_{est}$ = atrazine estimated. $[Atr]_{meas}$ = atrazine measured. $[Metol]_{est}$ = metolachlor estimated. $[Metol]_{meas}$ = metolachor measured.

ing herbicide application than those from F1 (table 4). Except in 1999 and 2000, herbicide concentrations from F2 were substantially larger than those from F1, particularly for the first few events. For the first event that occurred in 1999, atrazine concentration from F1 was slightly larger than that measured from F2. For this event, metolachlor concentration measured from F1 was more than 50% greater than that from F2, although metolachlor was applied to F2 11 days after it was applied to F1 (table 4). One of the reasons for the larger herbicide concentration from the mulch-tilled field for this event could be due to smaller volume of runoff measured from F1 compared to that from F2. In 2000, metolachlor concentrations from both fields were relatively low during the sampling period, even for the first event that occurred within a week of application

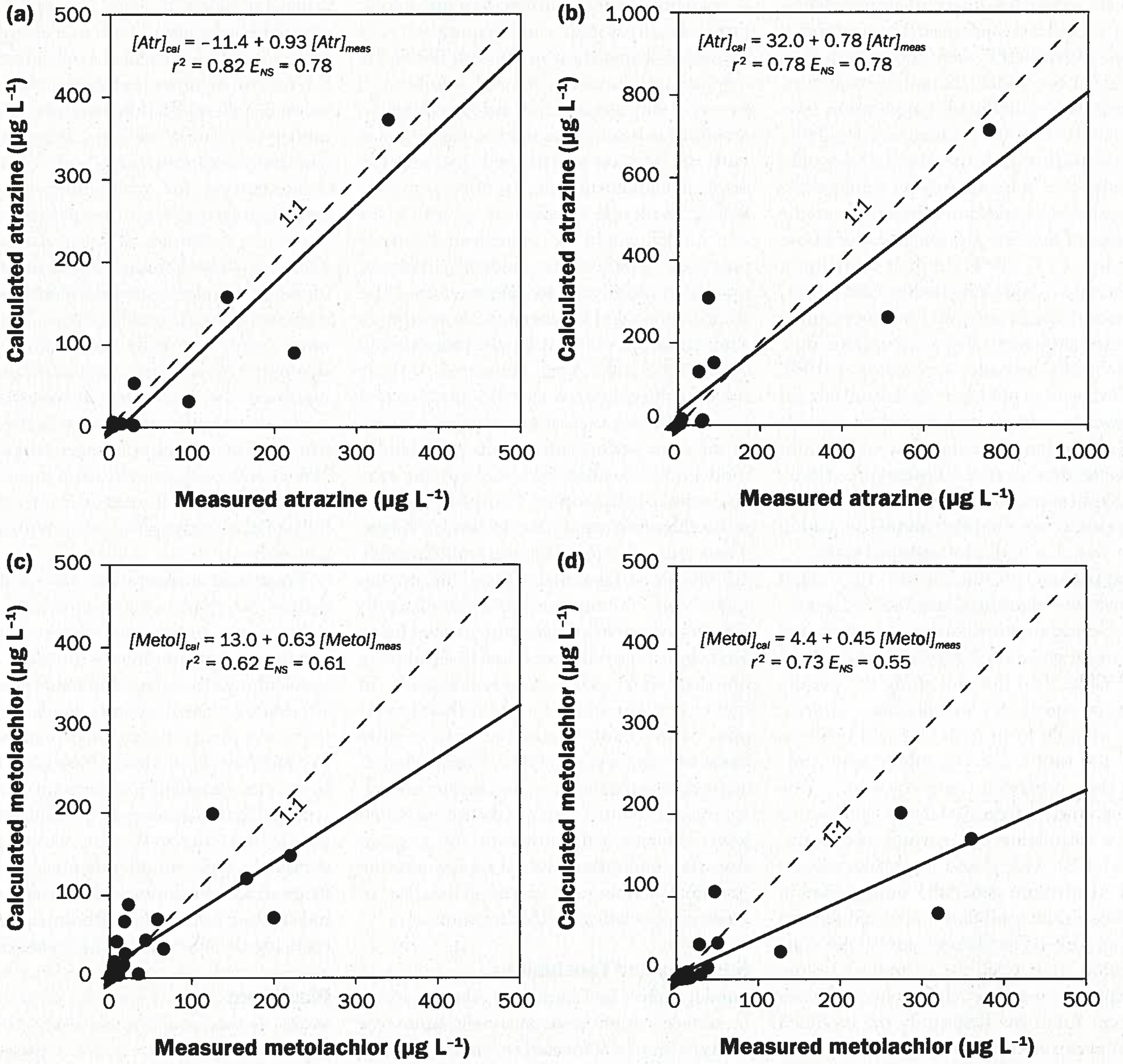
Overall, the method of application and time of runoff events relative to chemical application were important factors controlling herbicide concentrations in surface runoff. These observations corroborate the findings from plot data reported by Ghidey et al. (2005).

Modeling Herbicide Concentrations in Runoff. The applicability of the plot-scale generalized exponential model developed by Ghidey et al. (2005) was tested at the field scale. The plot model coefficients (α and κ) given in table 2 were used to calculate atrazine and metolachlor concentrations from F1 and F2. The performance of the model in calculating atrazine concentrations from both F1 and F2 was good (figure 3 and table 5). The r^2 and E_{NS} values for atrazine were 0.70 and 0.64 for F1 and were 0.74 and 0.73 for F2, respectively. These r^2 and E_{NS} values were similar to those obtained at the plot scale, 0.68 and 0.67 for CS1 and 0.80 and 0.79 for CS2, respectively (table 5). These results implied that the processes involved in the transport of atrazine to surface runoff at the field-scale study were similar to those at the plot-scale study. Thus, for atrazine, the exponential decay model was not scale dependent.

The performance of the plot-scale model in calculating metolachlor concentrations from F1 and F2 was poor. In the plot study, the performance of the model in calculating metolachlor concentrations had been good for CS1 (r^2 = 0.71 and E_{NS} = 0.70) whereas performance of the model in estimating metolachlor from F1 was poor (r^2 = 0.41 and E_{NS} = –0.13). This was mainly due to one event that occurred six days after application in 2001, where the measured metolachlor concentration was very low (125 μg L⁻¹), and the model greatly overestimated it (401 μg L⁻¹). Excluding this event, model performance in calculating metolachlor concentration for F1 was substantially improved, with r^2 = 0.59 and E_{NS} = 0.59. The model

Figure 4

Comparison of atrazine and metolachlor concentrations measured at Field 1 (F1) and Field 2 (F2) to those calculated using the coefficients of the modified model (equation 2) generated using the plot-scale data: (a) atrazine in F1, (b) atrazine in F2, (c) metolachlor in F1, and (d) metolachlor in F2.



Notes: $[Atr]_{cal}$ = atrazine calculated. $[Atr]_{meas}$ = atrazine measured. $[Metol]_{cal}$ = metolachlor calculated. $[Metol]_{meas}$ = metolachor measured.

did not perform well in estimating metolachlor from no-tillage (CS2) in the plot study. The performance of the model in estimating metolachlor from F2 was better than CS2, but it still substantially underestimated large concentrations (figure 3).

Throughout the study period, atrazine concentrations measured from the plot and field-scale studies were high for the first few events and declined rapidly within six to eight weeks following application. Because of this, the model performed well in calculating atrazine concentrations from F1 and F2. However, this pattern was not always seen in metolachlor concentrations measured from both fields. For instance, in 2001, metolachlor concentrations measured from F1 for the first event that occurred six days after application was 125 μg L^{-1}. In 2000, metolachlor concentration measured from F1 and F2 were relatively low even for the events that occurred within a few days after application (table 4). The model greatly overestimated these low concentrations measured within 10 days following application.

On the other hand, in 1997, metolachlor concentrations measured from F1 20 and 23 days following application were 200 and 220 μg L^{-1}. Metolachlor concentrations measured from F2 16 and 12 days after application in 1997 and 1998, respectively, were also high (320 and 360 μg L^{-1}). The model underestimated metolachlor concentration for these events (figure 3). These high values could be caused by lower microbial degradation at colder temperature. These events at the end of May 1997 were the only ones in our dataset for which the average soil temperature since herbicide application was less than 10°C (50°F). Dinelli et al. (2000) studied atrazine and metolachlor degradation rates as a function of soil temperature and reported significant differences in the half-lives of atrazine and metolachlor above and below 15°C (59°F). In their study, lower temperature significantly decreased degradation rate. Because of the low temperature and assumedly low degradation rate during the two weeks after application in 1997, more herbicide could have been available for transport to surface runoff, and as a result, metolachlor concentrations were high for the events that occurred almost three weeks after application. To evaluate the effect of temperature, the modified model (equation 2) was tested at both plot and field scales.

Comparison of the r^2 and E_{NS} values obtained in calculating atrazine and metolachlor concentrations from the plots and fields using equation 2 is presented in figure 4 and table 5. In the plot study, the performance of equation 2 in calculating atrazine concentrations from both CS1 and CS2 was good, and the r^2 and E_{NS} values were similar to those obtained using equation 1. The modified model (equation 2) also performed well in calculating metolachlor concentration for CS1 with r^2 and E_{NS} values slightly higher than those generated using equation 1. Although the modified model still did not perform well in calculating metolachlor concentration from CS2, the r^2 and E_{NS} values were almost two times those obtained with equation 1. For the field study, the modified model performed better in calculating atrazine and metolachlor concentrations from both F1 and F2 than those generated using equation 1 (table 5). In general, using cumulative soil and air temperature (T_{cum}) instead of days after application improved the performance of the model in calculating atrazine and metolachlor concentrations, particularly in the field-scale study.

Although the datasets on plots and fields were slightly different for CS1, CS2, F1, and F2 in terms of application date and herbicide rates, the atrazine models developed with plot data performed well on the plots and fields. These models implicitly represent the processes of herbicide degradation, sorption to soil, and transport by runoff. Herbicide degradation is the combination of abiotic processes (hydrolysis and photolysis) and biological degradation in the soil. Herbicide sorption in these soils can reach equilibrium in a very short period. For instance, atrazine sorption in batch equilibration experiments with the Mexico soil showed that sorption reached equilibrium in 24 hours (unpublished). Both the coefficients α and κ for our model would be influenced by these processes, which were evidently different for mulch tillage and no-tillage systems. The coefficients α and κ generated for atrazine in a mulch-tillage system using the plot data and equations 1 and 2 were compared to those for a no-tillage system. Coefficients obtained for metolachlor were not compared because of the poor performance of the metolachlor model on a no-tillage system. Thus, for atrazine, the coefficient α for no-tillage was more than four times that for mulch tillage. The κ value for no-tillage was approximately 1.3 times that for mulch tillage. This implies higher concentrations at similar runoff depths from no-tillage fields than mulch-tilled fields. However, it also implies faster dissipation in no-tillage fields. Thus, the model results in higher concentrations for the no-tillage system when runoff events occur soon after herbicide application. Once that period is elapsed, the greater κ value in the no-tillage model results in the prediction of much lower atrazine concentrations for a given day after application, indicating less atrazine available for transport in runoff because of greater degradation and/or sorption.

Summary and Conclusions

Surface runoff and herbicide concentrations in surface runoff were measured from two fields (F1 and F2) located in the claypan soil region of north-central Missouri from 1997 to 2001. Corn was planted during the odd years, and soybean was planted during the even years. Mean surface runoff measured during the CGS period from no-tillage and mulch tillage were similar. The percentages of applied atrazine and metolachlor transported to surface runoff from no-tillage were 3.2 and 2.0 times those from mulch tillage, respectively. Throughout the study period, 1.0% and 3.2% of the total atrazine and 1.0% and 2.0% of the total metalochlor applied to F1 and F2 were lost to surface runoff, respectively.

An exponential decay model, previously tested for plot-scale data, was evaluated for the field-scale data. The model calculates atrazine and metolachlor concentrations as a function of time after application, runoff volume, and application rate. The plot-scale model performed well in calculating atrazine concentrations from both F1 and F2, demonstrating the scale independence of atrazine transport and the validity of applying plot-scale studies to larger scales for this herbicide. However, the performance of the model in calculating metolachlor concentrations was poor. A modification of the model using cumulative daily temperature instead of number of days since application markedly improved the results for metolachlor. This could indicate the need to study the degradation of metolachlor at lower temperatures and if confirmed, it could affect management recommendations for metolachlor, especially in late fall or early spring when temperatures are cool.

These case studies at the field scale confirmed the results of the plot-scale studies (Ghidey et al. 2005). For claypan soils, atrazine and metolachlor losses from no-tillage, where herbicides were surface applied, were generally higher than from mulch tillage, where herbicides were typically incorporated. From a conservation point of view, soil-applied herbicides should be incorporated for soils with restrictive layers and especially in soils of the Central Claypan Region because of their extremely high runoff potential. The challenge resides in finding ways to incorporate soil-applied herbicides without significantly reducing the amount of crop residues.

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